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14. ABSTRACT Our research project that was supported by the Army Research Office sought to develop improved metal-organic film growth precursors for Pb- and Ba-containing materials, lanthanide-containing materials, and semiconductors that contain small clusters of magnetic elements within the semiconductor matrix. These materials encompass a broad range of military and civilian applications, and their successful development will literally change the way we live. More broadly, we sought to develop chemical insight into precursor structures that allowed maximum volatility to be obtained for a desired element-containing molecule, while also matching the growth chemistry of the precursor to that of the desired material. This					
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Report Title

ABSTRACT

Our research project that was supported by the Army Research Office sought to develop improved metal-organic film growth precursors for Pb- and Ba-containing materials, lanthanide-containing materials, and semiconductors that contain small clusters of magnetic elements within the semiconductor matrix. These materials encompass a broad range of military and civilian applications, and their successful development will literally change the way we live. More broadly, we sought to develop chemical insight into precursor structures that allowed maximum volatility to be obtained for a desired element-containing molecule, while also matching the growth chemistry of the precursor to that of the desired material. This report describes progress that was made during the project in our precursor development efforts as well as the use of our new precursors in the growth of thin film materials. Specific objectives included: (1) synthesis of volatile precursors to $\text{PbxBa}_{1-x}\text{TiO}_3$, which should allow the growth of films by MOCVD and of sub-micron sized three-dimensional structures through laser-assisted CVD growth; (2) synthesis of volatile polymetallic Cr, Mn, and other magnetic element precursors that can be used to dope semiconductors with multimetallic magnetic nanoscale structures. Such multimetallic magnetic sites are thought to be responsible for the high magnetic ordering temperatures that have been observed in many magnetic semiconductors such as GaN:Mn ; and (3) development of improved volatile lanthanide complexes to be used in the doping of semiconductors.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. "Synthesis, Structure, and Ligand Redistribution Equilibria of Mixed Ligand Complexes of the Heavier Group 2 Elements Containing Pyrazolato and Beta-Diketiminato Ligands," H. M. El-Kaderi, M. J. Heeg, and C. H. Winter, *Eur. J. Inorg. Chem.* 2005, 2081-2088.
2. "Synthesis, Structure, and Properties of Monomeric Strontium and Barium Complexes Containing Terminal eta²-3,5-Di-tert-butylpyrazolato Ligands," H. M. El-Kaderi, M.J. Heeg, and C.H. Winter, *Polyhedron* 2005, 24, 645-653.
3. "Atomic Layer Deposition of Tungsten Carbonitride Thin Films from a New Metalorganic Precursor," C. L. Dezelah IV, O. M. El-Kadri, M. J. Heeg, L. Niinistö, and C. H. Winter, *Proc. Electrochem. Soc.* 2005, 2005-09, 563-574.
4. "Synthesis, Structure, and Properties of Volatile Lanthanide Complexes Containing Amidinate Ligands: Application for Er_2O_3 Thin Film Growth by Atomic Layer Deposition," J. Päiväsaari, C. L. Dezelah IV, D. Back, H. M. El-Kaderi, M. J. Heeg, M. Putkonen, L. Niinistö, and C. H. Winter, *J. Mater. Chem.* 2005, 15, 4224-4233.
5. "Metallic Materials Deposition: Metal-Organic Precursors," C. H. Winter, W. Zheng, and H. M. El-Kaderi, *Encyclopedia of Inorganic Chemistry-II*, Wiley: Chichester, 2005, Volume 5, pp. 3121-3144.
6. "Complexes of the Heavier Alkaline Earth Metals Containing Beta-Diketiminato and Iodide Ligand Sets," H. M. El-Kaderi, M.J. Heeg, and C.H. Winter, *Polyhedron* 2006, 25, 224-234.
7. "Atomic Layer Deposition of Ga_2O_3 Films from a Dialkylamido-Based Precursor," C. L. Dezelah IV, J. Niinistö, K. Arstila, L. Niinistö, and C. H. Winter, *Chem. Mater.* 2006, 18, 471-475.
8. "Atomic Layer Deposition of Tungsten(III) Oxide Thin Films From $\text{W}_2(\text{NMe}_2)_6$ and Water. Oxidation State Control in the Thin Film Material Through Precursor Design," C. L. Dezelah IV, O. M. El-Kadri, I. Szilágyi, J. M. Campbell, K. Arstila, L. Niinistö, and C. H. Winter, *J. Am. Chem. Soc.* 2006, 128, 9638-9639.
9. "Atomic Layer Deposition of Rare Earth Oxides," J. Päiväsaari, J. Niinistö, P. Myllymäki, C. L. Dezelah IV, C. H. Winter, M. Putkonen, M. Nieminen, and L. Niinistö, *Top. Appl. Phys.* 2007, 106, 15-32.
10. "The Growth of $\text{Er}_x\text{Ga}_{2-x}\text{O}_3$ films by Atomic Layer Deposition from Two Different Precursor Systems," C. L. Dezelah IV, P. Myllymäki, J. Päiväsaari, K. Arstila, L. Niinistö, and C. H. Winter, *J. Mater. Chem.* 2007, 17, 1308-1315.
11. "A Pyrazolate-Based Metalorganic Tantalum Precursor That Exhibits High Thermal Stability and Its Use in the Atomic Layer Deposition of Ta_2O_5 ," C. L. Dezelah IV, M. K. Wiedmann, K. Mizohata, R. J. Baird, L. Niinistö, and C. H. Winter, *J. Am. Chem. Soc.* 2007, 129, 12370-12371.

Number of Papers published in peer-reviewed journals: 11.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. “Synthesis, Structure, and Atomic Layer Deposition Film Growth Studies of Tris(amidinate)lanthanide(III) Precursors,” C. L. Dezelah IV, D. Back, H. M. El-Kaderi, M. J. Heeg, C. H. Winter, J. Päiväsaari, M. Putkonen, and L. Niinistö, ALD 2004, Helsinki, Finland, August 16-18, 2004, Poster #8.
2. “Sandwich Complexes of the Group 2 Elements Containing Beta-Diketiminato Ligands,” H. M. El-Kaderi, M. J. Heeg, and C. H. Winter, 37th Inorganic Discussion Weekend, Queens University, Kingston, Ontario, November 6-7, 2004, Talk #B08.
3. “Atomic Layer Deposition of Rare Earth Oxide Thin Films Exploiting Different Precursor Chemistries,” L. Niinistö, M. Putkonen, J. Päiväsaari, J. Niinistö, A. Kosola, M. Nieminen, C. L. Dezelah IV, and C. H. Winter, 24th Rare Earth Research Conference, Keystone, Colorado, June 26-30, 2005, poster presentation.
4. “Atomic Layer Deposition (ALD) of High Quality Ga₂O₃ Thin Films from a Dimeric Dialkylamido-Bridged Gallium Complex,” C. L. Dezelah IV, J. Niinistö, M. Putkonen, K. Arstila, C. H. Winter, and L. Niinistö, ALD 2005, San Jose, California, August 7-10, 2005, poster presentation.
5. “Complexes of Group 2 Elements Containing Beta-Diketiminato Ligands,” C. H. Winter, H. M. El-Kadri, and M. J. Heeg, American Chemical Society National Meeting, Washington, D.C., August 28-31, 2005, Talk #INOR-7, in the symposium “Beta-Diketiminates: A Renaissance of Reaction Chemistries”.
6. “New Precursors for the Growth of Metal Nitride and Oxide Films by Atomic Layer Deposition,” Professor Lauri Niinistö Retirement Symposium, Helsinki University of Technology, May 9, 2007.
7. “A Pyrazolate-Based Metalorganic Tantalum Precursor Exhibiting High Thermal Stability and its Use in the Atomic Layer Deposition of Ta₂O₅,” C. H. Winter, C. L. Dezelah IV, M. K. Wiedmann, K. Mizohata, R. J. Baird, and L. Niinistö, 7th International Conference on Atomic Layer Deposition, San Diego, California, June 24-27, 2007.

Number of Presentations: 7.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Hani M. El Kadri	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Charles L. Dezelah IV	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PhDs

NAME

Likitha Seneviratne

Hani M. El-Kaderi

Total Number:

2

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

A paper was published that described the synthesis, structure, and properties of calcium, strontium, and barium complexes that contain b-diketiminato and pyrazolate ligands (“Synthesis, Structure, and Ligand Redistribution Equilibria of Mixed Ligand Complexes of the Heavier Group 2 Elements Containing Pyrazolato and β -Diketiminato Ligands,” H. M. El-Kaderi, M. J. Heeg, and C. H. Winter, *Eur. J. Inorg. Chem.* **2005**, 2081-2088). Treatment of $M(N(SiMe_3)_2)_2(THF)_2$ ($M = Ca, Sr, Ba$) with various stoichiometries of *N-tert*-butyl-4-(*tert*-butylimino)-2-penten-2-amine ($L^{tBu}H$) and 3,5-di-*tert*-butylpyrazole (tBu_2pzH) afforded $[(\eta^2-tBu_2pz)Ca(\mu-\eta^5:\eta^2-tBu_2pz)(\mu-\eta^2:\eta^2-tBu_2pz)Ca(\eta^5-L^{tBu})]$ (17%), $[Sr(\mu-\eta^5:\eta^2-tBu_2pz)(\eta^5-L^{tBu})]_2$ (50%), and $[Ba(\mu-\eta^5:\eta^2-tBu_2pz)(\eta^5-L^{tBu})]_2$ (66%) as colorless crystalline solids. The formulations of the new complexes were assigned from spectral and analytical data and by X-ray crystal structure determinations. In the solid state, $[(\eta^2-tBu_2pz)Ca(\mu-\eta^5:\eta^2-tBu_2pz)(\mu-\eta^2:\eta^2-tBu_2pz)Ca(\eta^5-L^{tBu})]$ exists as a dimer that is held together by $\mu-\eta^5:\eta^2$ - and $\mu-\eta^2:\eta^2$ -pyrazolato ligands, with a terminal η^2-tBu_2pz ligand on one calcium ion and an η^5-L^{tBu} ligand on the other. The dimeric structures of $[Sr(\mu-\eta^5:\eta^2-tBu_2pz)(\eta^5-L^{tBu})]_2$ and $[Ba(\mu-\eta^5:\eta^2-tBu_2pz)(\eta^5-L^{tBu})]_2$ are connected by two $\mu-\eta^5:\eta^2$ -pyrazolato ligands, and the coordination sphere of each metal ion is capped with an η^5-L^{tBu} ligand. In toluene solution, $[(\eta^2-tBu_2pz)Ca(\mu-\eta^5:\eta^2-tBu_2pz)(\mu-\eta^2:\eta^2-tBu_2pz)Ca(\eta^5-L^{tBu})]$ exists as an equilibrium mixture of at least four compounds. In toluene solution, $[Sr(\mu-\eta^5:\eta^2-tBu_2pz)(\eta^5-L^{tBu})]_2$ exists in equilibrium with $Sr(\eta^5-L^{tBu})_2$ and $Sr_4(tBu_2pz)_8$. A van't Hoff analysis of this equilibrium between 46-104 °C afforded $\Delta H^\circ = 22.2 \pm 0.7$ kcal/mol, $\Delta S^\circ = 43.7 \pm 1.9$ cal/mol-K, and $\Delta G^\circ(298\text{ K}) = 9.2 \pm 0.9$ kcal/mol. $[Ba(\mu-\eta^5:\eta^2-tBu_2pz)(\eta^5-L^{tBu})]_2$ exists in toluene solution as a single, pure species between -60 and +80 °C. The overall results suggest that the η^5-L^{tBu} ligand is better at saturating the coordination sphere of the metal ion to which it coordinates than is the tBu_2pz ligand, and is suggested as a more promising ligand for the construction of practical, volatile chemical vapor deposition film growth precursors.

A paper was published that described the synthesis, structure, and properties of strontium and barium pyrazolate complexes (“Synthesis, Structure, and Properties of Monomeric Strontium and Barium Complexes Containing Terminal η^2 -3,5-Di-*tert*-butylpyrazolato Ligands,” H. M. El-Kaderi, M.J. Heeg, and C.H. Winter, *Polyhedron* **2005**, 24, 645-653). Treatment of $Ba(N(SiMe_3)_2)_2(THF)_2$ with tetraglyme or triglyme (1 equiv) followed by 3,5-di-*tert*-butylpyrazole (2 equiv) in toluene afforded bis(3,5-di-*tert*-butylpyrazolato)(tetraglyme)barium (68%) and bis(3,5-di-*tert*-butylpyrazolato)(triglyme)barium (32%) as colorless solids after crystallization from hexane. Similar treatment of $Sr(N(SiMe_3)_2)_2(THF)_2$ with tetraglyme, triglyme, or *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (1 equiv) followed by 3,5-di-*tert*-butylpyrazole (2 equiv) in toluene afforded bis(3,5-di-*tert*-butylpyrazolato)(tetraglyme)strontium (50%), bis(3,5-di-*tert*-butylpyrazolato)(triglyme)strontium (73%), and bis(3,5-di-*tert*-butylpyrazolato)-(PMDETA)strontium(II) (64%), respectively, as colorless solids. The X-ray crystal structures of these complexes revealed monomeric molecules in which each metal coordination sphere is capped by one neutral polydentate ligand and two terminal η^2 -pyrazolato ligands. Volatility studies showed that these complexes fail to sublime, and rather decompose under sublimation conditions with neutral ligand loss for the barium complexes and loss of the neutral ligands and 3,5-di-*tert*-butylpyrazole for the strontium complexes.

A paper was published in *Proc. Electrochem. Soc.* that described the ALD growth and characterization of tungsten carbonitride thin films from a new metalorganic precursor (“Atomic

Layer Deposition of Tungsten Carbonitride Thin Films from a New Metalorganic Precursor,” C. L. Dezelah IV, O. M. El-Kadri, M. J. Heeg, L. Niinistö, and C. H. Winter, *Proc. Electrochem. Soc.* **2005**, 2005-09, 563-574). The principal investigator was an invited speaker at EUROCV-15 (September 4-9, 2005 in Bochum, Germany), and this manuscript was published in an issue containing papers from this meeting. Treatment of $W(NtBu)_2(NHtBu)_2$ with two equivalents of 3,5-di-*tert*-butylpyrazole (tBu_2pzH) afforded $W(NtBu)_2(tBu_2pz)_2$ in 93% yield. $W(NtBu)_2(tBu_2pz)_2$ was characterized by spectral and analytical techniques, and by single crystal X-ray crystallography. It sublimes without decomposition at 115 °C (0.03 Torr). Atomic layer deposition film growth trials were carried out between 350-500 °C using $W(NtBu)_2(tBu_2pz)_2$ and ammonia. A film grown at 450 °C had a composition of $WN_{1.7}C_{1.5}O_{0.61}H_{0.72}$ as determined by ion beam analyses. Between 400-450 °C, the growth rate increased with substrate temperature. At 450 °C, the film growth rate was independent of the pulse length of $W(NtBu)_2(tBu_2pz)_2$, demonstrating the surface controlled nature of the growth process. The film thicknesses had a linear dependence on the number of deposition cycles. Film resistivities ranged from 200-230 microhm cm for 8-28 nm thick films. The as-deposited films remained amorphous at temperatures below 800 °C, but crystallized to a mixture of tetragonal WO_3 and β - W_2N at ≥ 800 °C.

A paper was published that described the synthesis of a range of volatile lanthanide amidinate complexes, as well as use of an erbium precursor for the growth of Er_2O_3 films by atomic layer deposition (“Synthesis, Structure, and Properties of Volatile Lanthanide Complexes Containing Amidinate Ligands: Application for Er_2O_3 Thin Film Growth by Atomic Layer Deposition,” J. Päiväsari, C. L. Dezelah IV, D. Back, H. M. El-Kaderi, M. J. Heeg, M. Putkonen, L. Niinistö, and C. H. Winter, *J. Mater. Chem.* **2005**, 15, 4224-4233). Treatment of anhydrous rare earth chlorides with three equivalents of lithium 1,3-di-*tert*-butylacetamidinate (prepared *in situ* from the di-*tert*-butylcarbodiimide and methyllithium) in tetrahydrofuran at ambient temperature afforded $Ln(tBuNC(CH_3)N^tBu)_3$ ($Ln = Y, La, Ce, Nd, Eu, Er, Lu$) in 57-72% isolated yields. X-ray crystal structures of these complexes demonstrated monomeric formulations with distorted octahedral geometries about the lanthanide(III) ions. These new complexes are thermally stable at >300 °C, and sublime without decomposition between 180-220 °C/0.05 Torr. The atomic layer deposition of Er_2O_3 films was demonstrated using $Er(tBuNC(CH_3)N^tBu)_3$ and ozone with substrate temperatures between 225-300 °C. The growth rate increased linearly with substrate temperature from 0.37 Å/cycle at 225 °C to 0.55 Å/cycle at 300 °C. Substrate temperatures of >300 °C resulted in significant thickness gradients across the substrates, suggesting thermal decomposition of the precursor. The film growth rate increased slightly with erbium precursor pulse length between 1.0 s and 3.0 s, with growth rates of 0.39 Å/cycle and 0.51 Å/cycle, respectively. In a series of films deposited at 250 °C, the growth rates varied linearly with the number of deposition cycles. Time of flight elastic recoil analyses demonstrated slightly oxygen-rich Er_2O_3 films, with carbon, hydrogen, and fluorine levels of 1.0-1.9, 1.7-1.9, and 0.3-1.3 atomic percent, respectively, at substrate temperatures of 250 and 300 °C. Infrared spectroscopy showed the presence of carbonate, suggesting that the carbon and slight excess of oxygen in the films are due to this species. The as-deposited films were amorphous below 300 °C, but showed reflections due to cubic Er_2O_3 at 300 °C. Atomic force microscopy showed root mean square surface roughnesses of 0.3 and 2.8 nm for films deposited at 250 and 300 °C, respectively.

A major review article published in the *Encyclopedia of Inorganic Chemistry-II* (“Metallic Materials Deposition: Metal-Organic Precursors,” C. H. Winter, W. Zheng, and H. M. El-Kaderi, *Encyclopedia of Inorganic Chemistry-II*, Wiley: Chichester, **2005**, Volume 5, pp. 3121-3144.). Our review describes metal-organic precursors for the growth of metal-containing thin films by chemical vapor deposition methods. The major emphasis is on precursors that have been reported since 1994, and corresponds to a time of major growth in this field. Progress in the development of metal-organic precursors is documented for the main group, lanthanide, and group 4-11 elements. In the main group elements, there has been considerable research activity directed toward the identification of strontium and barium precursors, due both to the technological importance of mixed oxide phases and the inherent difficulties in obtaining volatile, thermally complexes of these large metal ions. Aluminum, gallium, and indium have also been the subject of intense investigation, due to the importance of many of phases containing these elements. The group 4 and 5 elements titanium, zirconium, hafnium, niobium, and tantalum have been the subject of considerable precursor development activity, due to the importance of several mixed oxide phases and the importance of zirconium and hafnium oxide for high permittivity gate materials in microelectronics devices. Growth of metal nitride films of these elements has also been an active area of research for use as barrier materials in microelectronics devices. The deposition of copper metal films from metal-organic precursors is driven by the urgent need for copper metallization procedures in microelectronics device manufacturing. The current state of metal-organic precursor development is presented for each of the other metallic elements.

A paper was published that reported the synthesis, structure, and properties of a series of calcium, strontium, and barium complexes containing β -diketiminato and iodide ligands (“Complexes of the Heavier Alkaline Earth Metals Containing β -Diketiminato and Iodide Ligand Sets,” H. M. El-Kaderi, M.J. Heeg, and C.H. Winter, *Polyhedron* **2006**, 25, 224-234). Treatment of $[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{tBu})\text{CH}_2\text{C}(\text{tBu})\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]$ ($\text{L}^{\text{Ar}}\text{H}$) with potassium hydride in tetrahydrofuran afforded $\text{K}(\eta^1\text{-L}^{\text{Ar}})(\text{THF})_3$ (89%) as a yellow crystalline solid after workup. The crystal structure of $\text{K}(\eta^1\text{-L}^{\text{Ar}})(\text{THF})_3$ revealed an open monomeric molecule in which the potassium ion is bonded to three tetrahydrofuran ligands and one η^1 - β -diketiminato ligand through one of the nitrogen atoms. Treatment of $\text{K}(\eta^1\text{-L}^{\text{Ar}})(\text{THF})_3$ with equimolar amounts of MI_2 ($\text{M} = \text{Ca}, \text{Ba}$) afforded $[\text{Ca}(\eta^5\text{-L}^{\text{Ar}})(\mu\text{-I})(\text{THF})_2]$ (62%) and $[\text{Ba}(\eta^2\text{-L}^{\text{Ar}})(\mu\text{-I})_2]$ (27%) as yellow crystalline solids. Treatment of $\text{M}(\eta^5\text{-L}^{\text{tBu}})_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$, $\text{L}^{\text{tBu}} = \text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu}^-$) with the corresponding metal iodide in tetrahydrofuran afforded $[\text{Ca}(\eta^5\text{-L}^{\text{tBu}})(\mu\text{-I})(\text{THF})_2]$ (68%), $[\text{Sr}(\eta^5\text{-L}^{\text{tBu}})(\mu\text{-I})(\text{THF})_2]$ (53%), and $[(\eta^5\text{-L}^{\text{tBu}})\text{Ba}(\mu\text{-I})(\mu\text{-}\eta^2\text{:}\eta^5\text{-L}^{\text{tBu}})\text{Ba}(\eta^5\text{-L}^{\text{tBu}})]_2$ (24%). Structural assignments for these complexes were based on spectral and analytical data as well as X-ray crystallography. $[\text{Ca}(\eta^5\text{-L}^{\text{tBu}})(\mu\text{-I})(\text{THF})_2]$ and $[\text{Sr}(\eta^5\text{-L}^{\text{tBu}})(\mu\text{-I})(\text{THF})_2]$ are dimers that are held together by bridging iodide ligands, while $[\text{Ba}(\eta^5\text{-L}^{\text{tBu}})(\mu\text{-I})(\mu\text{-}\eta^2\text{:}\eta^5\text{-L}^{\text{tBu}})\text{Ba}(\eta^5\text{-L}^{\text{tBu}})]_2$ is a tetramer containing two symmetrical dimeric units that are linked by two bridging iodide ligands. In benzene- d_6 solution, $[\text{Ca}(\eta^5\text{-L}^{\text{Ar}})(\mu\text{-I})(\text{THF})_2]$ and $[\text{Ba}(\eta^2\text{-L}^{\text{Ar}})(\mu\text{-I})_2]$ are stable toward ligand redistribution. $[\text{Ca}(\eta^5\text{-L}^{\text{tBu}})(\mu\text{-I})(\text{THF})_2]$ exists as mixtures of three species in toluene- d_8 , but the mixed ligand complex is strongly favored under the conditions studied. At 31.3 °C, the equilibrium constant for ligand redistribution of $[\text{Sr}(\eta^5\text{-L}^{\text{tBu}})(\mu\text{-I})(\text{THF})_2]$ to $\text{Sr}(\eta^5\text{-L}^{\text{tBu}})_2$ and $\text{SrI}_2(\text{THF})_2$ in toluene- d_8 was 5.3×10^{-5} M.

We published a paper that described the atomic layer deposition growth of Ga_2O_3 films from a new metalorganic precursor (“Atomic Layer Deposition of Ga_2O_3 Films from a

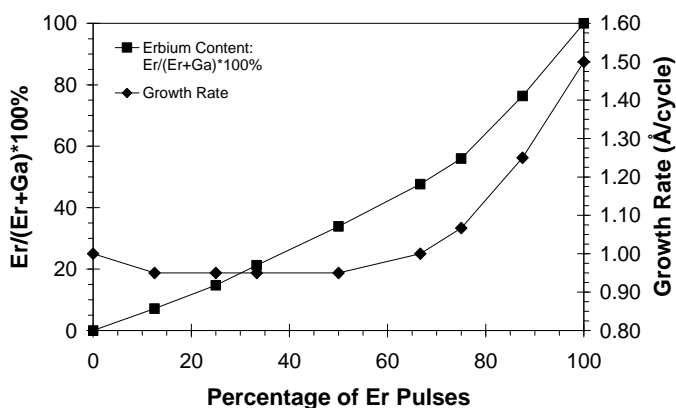
Dialkylamido-Based Precursor,” C. L. Dezelah IV, J. Niinistö, K. Arstila, L. Niinistö, and C. H. Winter, *Chem. Mater.* **2006**, *18*, 471-475). The atomic layer deposition growth of Ga₂O₃ films was demonstrated using Ga₂(NMe₂)₆ and water with substrate temperatures between 150 and 300 °C. At 250 °C, surface saturative growth was achieved with Ga₂(NMe₂)₆ vapor pulse lengths of ≥1.5 s. The growth rate was 1.0 Å/cycle at substrate temperatures between 170 and 250 °C. Growth rates of 1.1 and 0.89 Å/cycle were observed at 150 and 275 °C, respectively. In a series of films deposited at 250 °C, the film thicknesses varied linearly with the number of deposition cycles. Time of flight elastic recoil detection analyses demonstrated stoichiometric Ga₂O₃ films, with carbon, hydrogen, and nitrogen levels between 1.0-2.1, 4.8-5.4, and 0.6-0.9 atomic percent, respectively, at substrate temperatures of 170, 200, and 250 °C. The as-deposited films were amorphous, but crystallized to β-Ga₂O₃ films upon annealing between 700-900 °C under a nitrogen atmosphere. Atomic force microscopy showed root mean square surface roughnesses of 0.4 and 0.6 nm for films deposited at 170 and 250 °C, respectively.

We published a paper describing the growth of W₂O₃ films by atomic layer deposition (“Atomic Layer Deposition of Tungsten(III) Oxide Thin Films From W₂(NMe₂)₆ and Water. Oxidation State Control in the Thin Film Material Through Precursor Design,” C. L. Dezelah IV, O. M. El-Kadri, I. Szilágyi, J. M. Campbell, K. Arstila, L. Niinistö, and C. H. Winter, *J. Am. Chem. Soc.* **2006**, *128*, 9638-9639). The atomic layer deposition of W₂O₃ films was demonstrated employing W₂(NMe₂)₆ and water as precursors with substrate temperatures between 140 and 240 °C. At 180 °C, surface saturative growth was achieved with W₂(NMe₂)₆ vapor pulse lengths of ≥ 2 s. The growth rate was about 1.4 Å/cycle at substrate temperatures between 140 and 200 °C. Growth rates of 1.60 and 2.10 Å/cycle were observed at 220 and 240 °C, respectively. In a series of films deposited at 180 °C, the film thicknesses varied linearly with the number of deposition cycles. Time-of-flight elastic recoil analyses demonstrated stoichiometric W₂O₃ films, with carbon, hydrogen, and nitrogen levels between 6.3 and 8.6, 11.9 and 14.2, and 4.6 and 5.0 at. %, respectively, at substrate temperatures of 160, 180, and 200 °C. The as-deposited films were amorphous. Atomic force microscopy showed root mean square surface roughnesses of 0.7 and 0.9 nm for films deposited at 180 and 200 °C, respectively. The resistivity of a film grown at 180 °C was 8500 microhm cm.

We are coauthors on a review that describes the growth of lanthanide oxide films by atomic layer deposition (ALD). This review appeared in early 2007 (“Atomic Layer Deposition of Rare Earth Oxides,” J. Päiväsaari, J. Niinistö, P. Myllymäki, C. L. Dezelah IV, C. H. Winter, M. Putkonen, M. Nieminen, and L. Niinistö, *Top. Appl. Phys.* **2007**, *106*, 15-32). In particular, the review covers recent work from our laboratory on precursor selection and the attendant growth properties as a function of precursor structure. This manuscript is a collaborative effort with Professor Lauri Niinistö of the Helsinki University of Technology.

A paper was published (“The Growth of Er_xGa_{2-x}O₃ films by Atomic Layer Deposition from Two Different Precursor Systems,” C. L. Dezelah IV, P. Myllymäki, J. Päiväsaari, K. Arstila, L. Niinistö, and C. H. Winter, *J. Mater. Chem.* **2007**, *17*, 1308-1315) that described the ALD growth of the ternary material Er_xGa_{2-x}O₃ (0 ≤ x ≤ 2) from new precursors developed through our synthetic efforts. The ALD growth of Er_xGa_{2-x}O₃ thin films was demonstrated using two precursor systems: Er(MeCp)₃, Ga₂(NMe₂)₆, and water and Er(thd)₃, Ga(acac)₃, and ozone at substrate temperatures of 250 and 350 °C, respectively. Both processes provided uniform films and exhibited surface limited ALD-type growth. The value of x could be easily varied by selecting a pulsing sequence using an appropriate erbium to gallium precursor ratio. The Er(thd)₃/Ga(acac)₃/O₃ precursor system provided stoichiometric Er_xGa_{2-x}O₃ films with carbon,

hydrogen, nitrogen, and fluorine levels of <0.2, <0.2, <0.3, and 0.6-2.2 atom percent, respectively, as determined by Rutherford backscattering spectrometry (RBS) and time of flight-elastic recoil detection analysis (TOF-ERDA). The film growth rate was between 0.25 and 0.30 Å/cycle and varied as a function of the Er(thd)₃ to Ga(acac)₃ ratio. The effective permittivity of representative samples was 10.8-11.3. The Er(MeCp)₃/Ga₂(NMe₂)₆/H₂O precursor system provided nearly stoichiometric Er_xGa_{2-x}O₃ films with carbon, hydrogen, nitrogen, and fluorine levels between 2.0-6.1, 5.0-10.3, <0.3-0.7, and ≤0.1 atom percent, respectively, as determined by RBS and TOF-ERDA. The film growth rate was between 1.0 and 1.5 Å/cycle and varied as a function of the Er(MeCp)₃ to Ga₂(NMe₂)₆ ratio. The effective permittivity of representative samples was 9.2-10.4. The as-deposited films of both precursor systems were amorphous, but crystallized to either Er₃Ga₅O₁₂ or a mixture of β-Ga₂O₃ and Er₃Ga₅O₁₂ upon annealing between 900-1000 °C under a nitrogen atmosphere. Atomic force microscopy showed root mean square surface roughness of typical films was below 1.0 nm regardless of precursor system or film composition.



We published a paper describing the atomic layer deposition (ALD) growth of Ta₂O₅ thin films using *tert*-butylimidotris(3,5-di-*tert*-butylpyrazolato)tantalum and ozone as precursors at deposition temperatures between 250 and 500 °C (“A Pyrazolate-Based Metalorganic Tantalum Precursor That Exhibits High Thermal Stability and Its Use in the Atomic Layer Deposition of Ta₂O₅,” C. L. Dezelah IV, M. K. Wiedmann, K. Mizohata, R. J. Baird, L. Niinistö, and C. H. Winter, *J. Am. Chem. Soc.* **2007**, *129*, 12370-12371.). The process provided uniform films and exhibited a large ALD window between 300 and 450 °C, in which a constant growth rate of 0.30 Å/cycle was observed. Surface-limited growth was confirmed at 325 °C, as evidenced by a constant growth rate with increasing precursor dose as delivered by longer pulse lengths. Furthermore, the thickness of films deposited at 325 °C varied linearly with the number of deposition cycles, which demonstrates good thickness control typical of ALD growth. The process provided stoichiometric Ta₂O₅ films with carbon, hydrogen, and nitrogen levels of ≤ 1.0, ≤ 1.9, and ≤ 0.9 atomic percent, respectively, within the ALD temperature window as determined by time of flight-elastic recoil detection analysis. X-ray photoelectron spectroscopy measurements were consistent with the presence of Ta(V) and a stoichiometry of Ta₂O₅, with impurity elements below detection limits. All films were amorphous as deposited as determined by X-ray diffraction. This work is important because it demonstrates that the pyrazolate ligand can impart exceptional thermal stability to film growth precursors. Such thermal stability is a central requirement for ALD precursors to maintain the surface-limited growth mechanism. In

addition, low thermal stability is key problem with strontium, barium, and other high atomic weight metals. This paper was published in the *Journal of the American Chemical Society*, which is the most prestigious basic chemistry journal.

